



## Absorption spectroscopy in solid hydrogen: challenges to experimentalists and theorists

Adya P. Mishra<sup>a</sup>, T.K. Balasubramanian<sup>a,1</sup>, R.H. Tipping<sup>b,\*</sup>, Q. Ma<sup>c</sup>

<sup>a</sup>*Spectroscopy Division, Modular Laboratories, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India*

<sup>b</sup>*Department of Physics and Astronomy, University of Alabama, 206 Gallalee, Box 870324, Tuscaloosa, AL 35487-0324, USA*

<sup>c</sup>*Department of Applied Physics, Columbia University, and NASA Goddard Institute for Space Studies, 2800 Broadway, New York, NY 10025, USA*

Received 26 September 2003; accepted 17 October 2003

### Abstract

Hydrogen is the most abundant molecule in the universe, and over the years has provided a fundamental testing ground for both theory and experiment. By symmetry, isolated H<sub>2</sub> molecules do not have allowed dipole rotational or vibration-rotational spectra. However, when they interact in the gas, liquid, or solid, there are induced dipoles that can interact with radiation. In the solid because of the large lattice constant, these dipoles arise primarily from the long-range induction by multipole moments of one molecule with the polarizability in its neighbors. By analyzing the intensities, one is able to obtain experimental values for not only the quadrupole moment, but also for higher-order moments as well. In the present paper, we review only a very limited part of the extensive research that has been carried out; namely, that of solid H<sub>2</sub>, although extensive experimental and theoretical results for other phases and for other isotopes exist. Solid H<sub>2</sub> is a quantum crystal, in which the individual molecules undergo almost free rotation and vibration in the hcp lattice. This simplifies the identification of the observed transitions based on their frequencies calculated from well-known gaseous spectroscopic constants. Although high-resolution studies have revealed subtle effects such as crystal-field splittings, interferences between the allowed and induced dipoles in HD, structure of the phonon density of states, triple transitions, etc. we limit ourselves to only the zero-phonon single and double transitions in *para*-hydrogen, or for an isolated *ortho*-hydrogen molecule in a *para*-hydrogen environment. We review the extensive literature over the last four decades, and present comparisons between theory and experiment. From this analysis, we can draw a number of conclusions about the accuracy and consistency of the experimental data and the need for improvements in theory.

© 2003 Elsevier B.V. All rights reserved.

**Keywords:** Solid hydrogen; Zero-phonon transitions; Single and double transitions; Multipole-moment matrix elements; Phonon renormalization

### 1. Introduction

Molecular hydrogen for which pure rotational and rovibrational electric dipole transitions in the free state are symmetry-forbidden exhibits an infrared spectrum in the condensed phase caused by multipolar induction. Solid hydrogens (comprised of H<sub>2</sub>, D<sub>2</sub>, T<sub>2</sub>, HD, HT, and DT) are the archetypical molecular quantum crystals with fascinating low temperature behaviour. The special appeal of the solid hydrogens to spectroscopists stems from the fact that the gas phase property of quantized end-over-end molecular rotation persists in the solid down to 0 K with little change, and the spectral linewidth in the crystalline phase is

significantly narrower than the Doppler-limited gas phase spectral linewidth [1–3]. As a sensitive probe of the crystalline environment, the high-resolution spectroscopy of rotational and vibrational transitions of hydrogen molecules, and of embedded impurity atoms and molecules, gives information on the lattice vibrations and the relaxation dynamics of excited states in the solid (excitons), as well as many-body interactions in the condensed phase. The infrared absorption of the solid hydrogens typically consists of two parts: relatively sharp features, termed as ‘zero-phonon lines’, each accompanied by broad absorption contours on the higher frequency side, called ‘phonon branches’. The sharp lines are interpreted to be transitions among the levels associated with the internal degrees of freedom of one molecule (single transitions) or at least a pair of molecules (double and triple transitions) without any phonons being involved in the process. The accompanying

\* Corresponding author. Tel.: +1-205-348-5050; fax: +1-205-348-5051.

E-mail address: [rtipping@bama.ua.edu](mailto:rtipping@bama.ua.edu) (R.H. Tipping).

<sup>1</sup> Retired from Spectroscopy Division, BARC. Present address: A-21, Parmanu Nagar, Sector 4, Vashi, Navi Mumbai 400 703, India.

broad bands represent combination tones in which the absorption of a single photon excites an internal transition in one or more than one molecule with the simultaneous creation of phonons in the crystal.

The study of absorption intensities of zero-phonon transitions and their linewidths in the spectra of solid hydrogens, and comparisons between theory and experiment, have been the subject of extensive research [1–43] in the last four decades. There is, in general, more than a mere order-of-magnitude agreement between theory and experiment with just one or two exceptions, e.g. the  $Y_0(0)$  transition involving  $\Delta J = 8$  (caused by the  $2^8$ -pole moment). The discrepancies noticed between experimental and theoretical intensities of the transitions in some cases can be ascribed to: (i) the phonon renormalization factors ( $\xi$ ) appearing in the theoretical expressions of intensities, which correct the rigid lattice sums for the zero-point motions, are not known and their values are usually taken to be unity; (ii) inaccuracies of the multipole moment matrix elements, particularly for higher-order multipole moments  $Q_\ell$  ( $\ell \geq 6$ ,  $\ell$  being the order of the multipole), and for overtone transitions involving high  $v$ ; and (iii) limitations of the measurements. For some transitions, there are appreciable differences between independent experimental determinations of intensities, and for other transitions there is only a single measurement, so that the reproducibility of the results cannot be ascertained. In this paper, we make a comprehensive comparison between theory and experiment with an emphasis on the importance of phonon renormalization and the need for more accurate rovibrational matrix elements of multipole moments of  $H_2$ . We further discuss how one can determine the consistency of experimental results and the isotopic impurity concentration in a hydrogen crystal by intensity ratios for which the lattice sums cancel out. First, however, we feel it useful to give a brief review of the spectroscopy of solid hydrogens, and this is presented in Section 2.

## 2. Overview of experimental and theoretical findings

The Raman spectrum of liquid hydrogen was first observed by McLennan and McLeod [44] in 1929. In the solid phase, the first spectroscopic investigations were the infrared study of its fundamental vibrational band in 1955 and the observation of corresponding Raman spectra in 1956 by Allin and co-workers [45,46]. The experiments performed provided clear evidence for the nearly free rotation and vibration of the  $H_2$  molecules in the condensed phases. Subsequently, there were extensive studies performed for Raman spectra, and for the quadrupole-induced  $\Delta J = 0$  and 2 (Q and S) infrared transitions of solid- $H_2$  throughout the 1950s and 1960s. By extending the ideas of collision-induced absorption of diatomic gases under high pressure, the theory to explain the solid phase zero-phonon spectra was developed during

this period by Van Kranendonk [1], and the phonon branches by Poll and Van Kranendonk [47]. These experimental and theoretical studies are summarized in the review article by Van Kranendonk and Karl [7].

The last three decades have witnessed a flurry of activity in the absorption spectroscopy of solid hydrogens that opened up many opportunities and challenges for experimentalists and theorists alike. In a series of experiments carried out in several laboratories, the successively weaker transitions with  $\Delta J = 4, 6$ , and 8 have been measured in nearly pure *para*- $H_2$  crystal containing only trace amounts of *ortho*- $H_2$  impurity [8–23]. This era is marked by high-resolution and high-sensitivity infrared spectroscopy of solid *para*- $H_2$  with small *ortho*- $H_2$  impurities employing (among others) tunable difference frequency lasers and Fourier transform spectrometers, coupled with longer multipass cells. As illustrative of the limits of the sensitivity that could be achieved, the detection of the W transitions (that is  $\Delta J = J' - J'' = 6$ , caused by the  $2^6$ -pole, having an absorption coefficient  $\tilde{\alpha} \sim 10^{-19} \text{ cm}^3/\text{s}$ ) by the groups of Oka and Winnewissers, and of the Y ( $\Delta J = 8$ ) transitions (induced by the  $2^8$ -pole, having  $\tilde{\alpha} \sim 10^{-22} \text{ cm}^3/\text{s}$ ) by the Winnewissers' group may be cited [16–18]. The Winnewissers' group also reported, for the first time, the observation of triple transitions (a simultaneous excitation of three molecules by the absorption of a single photon) in solid  $H_2$  [22,23]. Such a transition, the triple  $S_0(0)$  transition in solid *ortho*- $D_2$  arising from mixing of rotational levels was predicted several years earlier [48], while the first triple transition was observed in the gaseous phase by Reddy et al. [49]. During this period the multipole-induced single and double transitions in other isotopomers  $D_2$  [6,24,25],  $T_2$  [26, 27], HD [28–30] and HT [26,27] and 'mixed isotopomer transitions' involving  $H_2$ -HD or  $D_2$ -HD pairs [25,28,30] were also observed. We note that for the heteronuclear molecules, transitions with odd  $\Delta J$  (1, 3, 5, etc.) are also allowed and have in fact been seen. The case of  $\Delta J = 1$  in HD, for instance the  $R_v(J)$  transitions, are of particular interest because of the existence of free molecular and induced dipoles of comparable strengths; these can interfere, resulting in a significant change of intensity depending on whether the interference is constructive or destructive [50].

Concurrently, there have been many attempts to correlate the experimental intensities with theoretical predictions based on the  $2^\ell$  multipolar induction mechanisms. While the long known quadrupole-induced transitions in  $H_2$  were considered by Van Kranendonk [4], those arising from higher-order ( $2^4$ ,  $2^6$ ,  $2^8$ ) multipole-induced transitions involving *para*- $H_2$  molecules were treated by Ma, Tipping, and Poll [32,33], extending the formalism developed in Ref. [4]. Later, the theory was further extended to the heteronuclear isotopomer HD by taking into account additional significant contributions from the shifted multipole-induced components arising from the non-coincidence of the centers of mass and charge [34–37]. The most comprehensive treatment of the absorption intensities of

zero-phonon single and double transitions in solid  $H_2$  and its isotopic heteronuclear variants, including mixed isotopomer transitions, was given by Balasubramanian, Mishra and co-workers [38–42]; these workers independently addressed the problem by following a more direct approach, starting from the relations for multipolar fields given by Gray [51], and by Poll and Tipping [32]. Apart from developing expressions of general validity applicable to a host of single and double transitions in solid *para*- $H_2$ , formulas were derived for the absorption by *ortho*- $H_2$  molecules (single transitions) and for double transitions involving an *ortho*- $H_2$ –*para*- $H_2$  pair dispersed in a *para*- $H_2$  matrix. Recently, Hinde [43] provided an induction mechanism, in terms of two- and three-body exchange- and dispersion-induced dipole moments, to explain the infrared activity of the forbidden pure vibrational double transitions  $Q_v(0) + Q_v(0)$  in solid *para*- $H_2$  observed first by Winnewissers' group [21].

In addition to the theoretical advances discussed above, accurate rotational and vibration-rotational matrix

elements for the multipole moments, as well as the isotropic and anisotropic polarizabilities of  $H_2$  and its isotopomers, required for the comparison of the experimental intensities to theory, were calculated by various researchers [52–61]. Other matrix elements of the form  $(r^n X)$ , where  $r$  is the internuclear separation,  $n = 1, 2, \dots$ , and  $X$  is either a multipole moment or polarizability function that are necessary to calculate the intensity contributions from the shifted moments in HD have also been calculated [34,36].

### 3. Comparison between theory and experiment

Among the various isotopic varieties of hydrogen most of the measurements of the multipole-induced spectra in the solid phase have centred on the most abundant isotopomer  $H_2$ . In Tables 1–3, we present a comparison of experimental and theoretical intensities of zero-phonon transitions in solid  $H_2$ . The theoretical intensities are calculated using

Table 1  
Comparison of theoretical and experimental integrated absorption coefficient  $\bar{\alpha}$  of typical zero-phonon single transitions in solid  $H_2$

Transition	Integrated absorption coefficient $\bar{\alpha}$ (cm <sup>3</sup> /s)		Measured by (Ref.)	Transition	Integrated absorption coefficient $\bar{\alpha}$ (cm <sup>3</sup> /s)		Measured by (Ref.)
	Theory	Experiment			Theory	Experiment	
$S_0(0)$	$7.32 \times 10^{-14}$	$5.2 \times 10^{-14}$ $8.1 \times 10^{-14}$	[16] [62]	$S_0(1)$	$4.46 \times 10^{-14}$	— <sup>a</sup>	
$U_0(0)$	$5.34 \times 10^{-16}$	$5.1(3) \times 10^{-16}$ $4.9 \times 10^{-16}$	[9] [30]	$U_0(1)$	$3.05 \times 10^{-16}$	$2.7 \times 10^{-16}$ $4.2(5) \times 10^{-16}$	[9] [22]
$W_0(0)$	$2.51 \times 10^{-19}$	$3.3 \times 10^{-19}$	[16]	$W_0(1)$	$1.42 \times 10^{-19}$	$4.4(4) \times 10^{-19}$	[17]
$Y_0(0)$	$1.18 \times 10^{-23}$	$2.5(3) \times 10^{-22}$	[17]	$Y_0(1)$	$6.72 \times 10^{-24}$	— <sup>a</sup>	
$[\Delta J = 10]_0(0)$	$2.27 \times 10^{-27}$	— <sup>a</sup>		$[\Delta J = 10]_0(1)$	$1.32 \times 10^{-27}$	— <sup>a</sup>	
$S_1(0)$	$1.91 \times 10^{-15}$	$3.3 \times 10^{-15}$ $4.5 \times 10^{-16}$	[5,16] [30]	$Q_1(1)$	$1.03 \times 10^{-15}$	— <sup>a</sup>	
$U_1(0)$	$6.48 \times 10^{-17}$	$6.6(6) \times 10^{-17}$ $7.50(10) \times 10^{-17}$ $5.5 \times 10^{-17}$	[16], [10] [18] [30]	$S_1(1)$	$1.00 \times 10^{-15}$	— <sup>a</sup>	
$W_1(0)$	$6.46 \times 10^{-20}$	$1.1 \times 10^{-19}$ $1.48(7) \times 10^{-19}$	[16] [18]	$U_1(1)$	$3.13 \times 10^{-17}$	$1.11(14) \times 10^{-17}$	[18]
$Y_1(0)$	$4.79 \times 10^{-24}$	$2.2(3) \times 10^{-23}$	[21]	$W_1(1)$	$3.07 \times 10^{-20}$	$1.1(2) \times 10^{-19}$	[17]
$[\Delta J = 10]_1(0)$	$1.26 \times 10^{-27}$	— <sup>a</sup>		$Y_1(1)$	$2.27 \times 10^{-24}$	— <sup>a</sup>	
$S_2(0)$	$4.22 \times 10^{-17}$	$1.2(2) \times 10^{-17}$ $1.1 \times 10^{-17}$ $2.3 \times 10^{-17}$	[21] [30] [15]	$[\Delta J = 10]_1(1)$	$5.97 \times 10^{-28}$	— <sup>a</sup>	
$U_2(0)$	$1.69 \times 10^{-21}$	$1.1(1) \times 10^{-19}$ $4.0 \times 10^{-19}$	[21] [30]	$Q_2(1)$	$1.57 \times 10^{-17c}$	$1.3(1) \times 10^{-17}$	[21]
$W_2(0)$	$6.95 \times 10^{-22}$	$8(2) \times 10^{-21}$	[22]	$S_2(1)$	$2.61 \times 10^{-17}$	$2.0(3) \times 10^{-17}$	[21]
$Y_2(0)$	$1.74 \times 10^{-25}$	— <sup>a</sup>		$U_2(1)$	$2.55 \times 10^{-20}$	— <sup>a</sup>	
$[\Delta J = 10]_2(0)$	$8.02 \times 10^{-29}$	— <sup>a</sup>		$W_2(1)$	$1.56 \times 10^{-22}$	— <sup>a</sup>	
$S_3(0)$	$1.16 \times 10^{-18}$	$3.0(3) \times 10^{-19}$	[22]	$Y_2(1)$	$5.00 \times 10^{-26}$	— <sup>a</sup>	
$U_3(0)$	$1.34 \times 10^{-20}$	— <sup>a</sup>		$[\Delta J = 10]_2(1)$	$2.41 \times 10^{-29}$	— <sup>a</sup>	
$W_3(0)$	$3.92 \times 10^{-23}$	— <sup>a</sup>		$Q_3(1)$	$3.20 \times 10^{-19c}$	— <sup>a</sup>	
$Y_3(0)$	$2.03 \times 10^{-27}$	— <sup>a</sup>		$S_3(1)$	$8.59 \times 10^{-19}$	— <sup>a</sup>	
$[\Delta J = 10]_3(0)$	$2.53 \times 10^{-31}$	— <sup>a</sup>		$U_3(1)$	$3.67 \times 10^{-21}$	— <sup>a</sup>	
				$W_3(1)$	$1.83 \times 10^{-23}$	— <sup>a</sup>	
				$Y_3(1)$	$1.49 \times 10^{-27}$	— <sup>a</sup>	
				$[\Delta J = 10]_3(1)$	$3.76 \times 10^{-31}$	— <sup>a</sup>	

Note that the experimental intensities of transitions  $U_0(1)$ ,  $U_1(1)$ ,  $W_0(1)$  and  $W_1(1)$  measured by Refs. [17,18,22] should be divided by 1.85 to get the correct value of  $\bar{\alpha}$ . See the text for explanation. Estimated experimental error, wherever available, is given in brackets and the correction factor  $g$  is set to 1 in Eq. (3).

<sup>a</sup> Not measured so far.

Table 2

Comparison of theoretical and experimental integrated absorption coefficient  $\bar{\alpha}$  of typical zero-phonon double transitions in solid *para* H<sub>2</sub>

Transition	Integrated absorption coefficient $\bar{\alpha}$ (cm <sup>3</sup> /s)		Measured by (Ref.)	Transition	Integrated absorption coefficient $\bar{\alpha}$ (cm <sup>3</sup> /s)		Measured by (Ref.)
	Theory	Experiment			Theory	Experiment	
$S_0(0) + S_0(0)$	$3.87 \times 10^{-14}$	$6.0 \times 10^{-14}$	[4]	$S_0(0) + Q_2(0)$	$5.27 \times 10^{-16}$	$4.5 \times 10^{-16}$	[30]
$S_1(0) + S_0(0)$	$4.86 \times 10^{-15}$	$4.5 \times 10^{-15}$	[13]			$4.9 \times 10^{-16}$	[15]
		$3.5(2) \times 10^{-15}$	[63]	$U_0(0) + Q_2(0)$	$1.56 \times 10^{-19}$	$1.4(4) \times 10^{-19}$	[21]
		$2.3 \times 10^{-15}$	[30]			$2.2 \times 10^{-19}$	[30]
$S_2(0) + S_0(0)$	$3.72 \times 10^{-17}$	$2.9(4) \times 10^{-17}$	[21]	$W_0(0) + Q_2(0)$	$3.61 \times 10^{-23}$	— <sup>a</sup>	
$S_3(0) + S_0(0)$	$2.67 \times 10^{-18}$	$1.7(1) \times 10^{-18}$	[22]	$Y_0(0) + Q_2(0)$	$8.27 \times 10^{-27}$	— <sup>a</sup>	
$S_1(0) + S_1(0)$	$7.92 \times 10^{-17}$	$3.8(2) \times 10^{-17}$	[21]	$S_1(0) + Q_2(0)$	$1.37 \times 10^{-17}$	$7.0(5) \times 10^{-18}$	[22]
		$4.3 \times 10^{-17}$	[30]			$9.3 \times 10^{-18}$	[30]
		$4.6 \times 10^{-17}$	[15]	$U_1(0) + Q_2(0)$	$1.89 \times 10^{-20}$	$2(1) \times 10^{-20}$	[22]
$S_2(0) + S_1(0)$	$3.34 \times 10^{-18}$	$2.2(1) \times 10^{-18}$	[22]	$W_1(0) + Q_2(0)$	$9.31 \times 10^{-24}$	— <sup>a</sup>	
		$2.9 \times 10^{-18}$	[30]	$Y_1(0) + Q_2(0)$	$3.37 \times 10^{-27}$	— <sup>a</sup>	
$S_0(0) + Q_1(0)$	$5.72 \times 10^{-14}$	$4.2 \times 10^{-14}$	[4]	$S_2(0) + Q_2(0)$	$3.04 \times 10^{-19}$	$9(1) \times 10^{-20}$	[22]
		$4.84(18) \times 10^{-14}$	[63]	$S_0(0) + Q_3(0)$	$1.00 \times 10^{-17}$	$7.8(3) \times 10^{-18}$	[22]
$U_0(0) + Q_1(0)$	$1.69 \times 10^{-17}$	$4.0 \times 10^{-17}$	[30]			$1.0 \times 10^{-17}$	[30]
$W_0(0) + Q_1(0)$	$3.92 \times 10^{-21}$	— <sup>a</sup>		$S_1(0) + Q_3(0)$	$2.61 \times 10^{-19}$	$1.7(2) \times 10^{-19}$	[22]
$Y_0(0) + Q_1(0)$	$8.97 \times 10^{-25}$	— <sup>a</sup>		$U_0(0) + S_0(0)$	$2.86 \times 10^{-17}$	$1.5(3) \times 10^{-17}$	[22]
$S_1(0) + Q_1(0)$	$1.49 \times 10^{-15}$	$9.1 \times 10^{-16}$	[30]	$W_0(0) + S_0(0)$	$6.63 \times 10^{-21}$	— <sup>a</sup>	
		$7.2 \times 10^{-16}$	[15]	$Y_0(0) + S_0(0)$	$1.52 \times 10^{-24}$	— <sup>a</sup>	
$U_1(0) + Q_1(0)$	$2.06 \times 10^{-18}$	$2.8(3) \times 10^{-18}$	[21]	$U_1(0) + S_0(0)$	$3.47 \times 10^{-18}$	$2.6 \times 10^{-18}$	[16]
		$2.9 \times 10^{-18}$	[30]	$W_1(0) + S_0(0)$	$1.71 \times 10^{-21}$	— <sup>a</sup>	
$W_1(0) + Q_1(0)$	$1.01 \times 10^{-21}$	— <sup>a</sup>		$Y_1(0) + S_0(0)$	$6.19 \times 10^{-25}$	— <sup>a</sup>	
$Y_1(0) + Q_1(0)$	$3.66 \times 10^{-25}$	— <sup>a</sup>		$U_0(0) + S_1(0)$	$2.25 \times 10^{-18}$	$1.6 \times 10^{-18}$	[16]
$S_2(0) + Q_1(0)$	$3.30 \times 10^{-17}$	$2.0(2) \times 10^{-17}$	[22]	$W_0(0) + S_1(0)$	$5.21 \times 10^{-22}$	— <sup>a</sup>	
		$4.3 \times 10^{-17}$	[30]	$Y_0(0) + S_1(0)$	$1.19 \times 10^{-25}$	— <sup>a</sup>	
$U_2(0) + Q_1(0)$	$5.36 \times 10^{-23}$	— <sup>a</sup>		$U_1(0) + S_1(0)$	$2.73 \times 10^{-19}$	$1.4(4) \times 10^{-19}$	[22]
$W_2(0) + Q_1(0)$	$1.09 \times 10^{-23}$	— <sup>a</sup>		$U_0(0) + S_2(0)$	$3.10 \times 10^{-21}$	$1.7(2) \times 10^{-20}$	[22]
$Y_2(0) + Q_1(0)$	$1.32 \times 10^{-26}$	— <sup>a</sup>					
$S_3(0) + Q_1(0)$	$9.06 \times 10^{-19}$	$4.1(4) \times 10^{-19}$	[22]				

Estimated experimental error, wherever available, is given in brackets.

<sup>a</sup> Not measured so far.

formulas developed in Refs. [38–40] in which the phonon renormalization factors  $\xi$  are taken as unity and the other parameters required are taken from Refs. [3,56,57]; these formulas are not repeated here.

The absorption spectra of solid D<sub>2</sub> and HD were also well studied, although these measurements are not as extensive as those for solid H<sub>2</sub>. Table III of Ref. [41] gives an extensive listing of theoretical intensities for transitions in solid HD and compares them with experimental findings whenever data are available. Similarly, for theoretical and experimental intensities of transitions in solid D<sub>2</sub>, we refer the reader to Table XI of Ref. [58].

As can be seen from Tables 1–3, the agreement between experimental and theoretical intensities varies from a few percent to more than an order-of-magnitude (a factor 21 for  $Y_0(0)$  transition mentioned previously). Although the quadrupolar  $S_v(0)$  transitions are most intense, there are noticeable differences between theory and experiment and the theoretical values are usually higher than the corresponding experimental ones. This can be partially attributed to the  $\xi$  factors that are more important for single transitions because the lattice sums are affected by the cancellation

effect [1,34]. For instance, the lattice sum  $S$  for  $S_v(0)$  transitions is given by

$$S = \sum_{ij} (a^2/a_i a_j)^4 P_3(\cos \theta_{ij}) \quad (1)$$

where  $a$  is the lattice spacing,  $a_i$  and  $a_j$  the distances from the central molecule to the neighbors  $i$  and  $j$ , and  $P_3$  is a Legendre polynomial with  $\theta_{ij}$  being the angle between  $a_i$  and  $a_j$ . By considering the phonon renormalization for only the 12 nearest neighbors in the hcp lattice, we find

$$S = \xi_{43}^2(0.835) - 0.529$$

This obviously depends sensitively on the value of  $\xi_{43}$ . One way to gain insight into the accuracy (or consistency) of the experimental measurements is to look at the ratios of intensities for the same rotational transition involving different vibrational states; in this case, the lattice sums will cancel. Consider, for instance,  $S_1(0)$  and  $S_2(0)$ . The ratio of the theoretical intensity values in Table 1 corresponds to  $(Q_{01}/Q_{02})^2 = 45$ , where  $Q_{01}$  and  $Q_{02}$  are the quadrupole moment matrix elements. By looking at the ratios of the two experimental intensities for  $S_1(0)$  and the three experimental values for  $S_2(0)$ , it is clear that the experimental value

Table 3

Comparison of theoretical and experimental integrated absorption coefficient  $\tilde{\alpha}$  of typical zero-phonon mixed double transitions in solid H<sub>2</sub>

Transition	Integrated absorption coefficient $\tilde{\alpha}$ (cm <sup>3</sup> /s)		Measured by (Ref.)
	Theory	Experiment <sup>a</sup>	
$Q_2(0) + Q_0(1)$	$4.73 \times 10^{-16}$	$3.8(1) \times 10^{-16}$	[21]
$Q_1(0) + Q_1(1)$	$1.69 \times 10^{-15}$	$1.2(2) \times 10^{-15}$ $1.4 \times 10^{-15b}$	[21] [15]
$Q_1(0) + Q_2(1)$	$2.75 \times 10^{-17}$	$1.4(2) \times 10^{-17}$	[22]
$Q_2(0) + Q_1(1)$	$1.56 \times 10^{-17}$	$7(1) \times 10^{-18}$	[22]
$Q_3(0) + Q_0(1)$	$9.00 \times 10^{-18}$	$1.6(5) \times 10^{-18}$	[22]
$Q_2(1) + S_0(0)$	$5.46 \times 10^{-16c}$	$1.9(2) \times 10^{-16}$	[21]
$Q_2(0) + S_0(1)$	$3.19 \times 10^{-16}$	$2.5(3) \times 10^{-16}$	[21]
$Q_1(0) + S_1(1)$	$7.55 \times 10^{-16}$	$1.1(2) \times 10^{-15}$ $2.3 \times 10^{-15b}$	[21] [15]
$Q_3(0) + S_0(1)$	$6.11 \times 10^{-18}$	$6(1) \times 10^{-18}$	[22]
$Q_3(1) + S_0(0)$	$1.09 \times 10^{-17}$	$2.2 \times 10^{-17}$	[30]
$Q_1(0) + S_2(1)$	$2.04 \times 10^{-17}$	$1.6(4) \times 10^{-17}$	[22]
$Q_2(0) + S_1(1)$	$6.97 \times 10^{-18}$	$1.3(3) \times 10^{-17}$	[22]
$S_0(0) + S_0(1)$	$4.69 \times 10^{-14}$	$6.0(6) \times 10^{-14}$	[22]
$U_0(0) + S_0(1)$	$1.74 \times 10^{-17}$	$1.6(8) \times 10^{-18}$	[22]
$S_2(1) + S_0(0)$	$2.27 \times 10^{-17}$	$5.8(8) \times 10^{-17}$	[21]
$S_1(1) + S_1(0)$	$8.37 \times 10^{-17}$	$9.5(8) \times 10^{-17}$ $4.9 \times 10^{-17}$	[21] [30]
$U_1(0) + Q_1(1)$	$2.18 \times 10^{-18}$	$2.4(4) \times 10^{-18}$	[21]
$U_1(1) + Q_1(0)$	$9.91 \times 10^{-19}$	$2.2(3) \times 10^{-18}$	[21]

Note that the experimental intensities of the transitions measured by Refs. [21,22] should be divided by 1.85 to get the correct value of  $\tilde{\alpha}$ . See the text for explanation.

<sup>a</sup> Estimated experimental error is given in brackets.

<sup>b</sup> The value of  $\tilde{\alpha}$  given here is 100 times the value given in Ref. [15] to account for correct density of absorbing species (*ortho*–*para* pair, with ~1% *ortho*-H<sub>2</sub> concentration).

<sup>c</sup> In Ref. [40], this value is misprinted as  $1.92 \times 10^{-16}$ .

of  $3.3 \times 10^{-15}$  for  $S_1(0)$  is definitely too high, and this is also consistent with the discussion above (following Eq. (1)) for the phonon renormalization effect. If we consider the other experimental intensity value for  $S_1(0)$  of  $4.5 \times 10^{-16}$ , the intensity value of  $1.1 \times 10^{-17}$  for  $S_2(0)$ , obtained by the same researchers, yields the intensity ratio 41 that comes closest to the theoretical ratio, showing thereby consistency in the two measurements. Similar consistency checks can be made for other ratios.

By comparing theoretical and experimental intensities for the  $U_v(0)$  transitions, one can conclude that the agreement is very good and that phonon renormalization is less important than for the  $S_v(0)$  transitions. For the higher multipolar transitions, the agreement is not as good, but this is what one would expect for two reasons: first, the transitions are progressively weaker and the experimental uncertainties are correspondingly larger; and second, the theoretical matrix elements for the higher multipolar moments are less accurate, especially for the higher vibrational transitions where larger cancellations occur (on account of the larger number of nodes associated with the higher vibrational wavefunctions).

Nevertheless, it is very useful to have approximate theoretical values for the intensities of even higher order multipolar induced transitions (not yet observed) and overtone transitions that can serve as a guide for experimentalists in order to decide on the most favorable experimental conditions under which to observe them.

Another way to check the consistency of the experimental data is to consider the intensity ratios of a single transition in *para*-H<sub>2</sub> and the corresponding one in *ortho*-H<sub>2</sub> (dispersed in *para*-H<sub>2</sub> crystal as small impurity) where even the matrix elements of the multipole moment or polarizability approximately cancel. In this case, for the integrated absorption coefficient  $\tilde{\alpha}$  (in cm<sup>3</sup>/s) ratio, one gets [39]

$$\frac{\tilde{\alpha}\{[\Delta J = \ell]_v(1)\}}{\tilde{\alpha}\{[\Delta J = \ell]_v(0)\}} \approx \frac{\ell + 1}{2\ell + 1} \quad (2)$$

According to Eq. (2), the intensity of the single transition  $[\Delta J = \ell]_v(1)$  in *ortho*-H<sub>2</sub> should be smaller than the corresponding *para*-H<sub>2</sub> transition  $[\Delta J = \ell]_v(0)$ . However, the Winnewisers' group obtained a value of  $\tilde{\alpha}$  for the  $U_1(1)$  transition that is larger than that of the  $U_1(0)$  transition [18]. Also,  $\tilde{\alpha}$  of the  $W_0(1)$  transition reported by the same group [17] is larger than that of  $W_0(0)$  transition reported by Oka's group [16]. After delving into the origin of this discrepancy we have found that its root-cause is ultimately traceable to an error in the theoretical value of  $\tilde{\alpha}$  for the transition  $Q_1(1)$  reported by Sears and Van Kranendonk [64] as  $1.9 \times 10^{-15}$  cm<sup>3</sup>/s. Winnewisers' group has used this value for assaying the *ortho*-H<sub>2</sub> concentration in their samples. The intensity of the  $Q_v(1)$  transition can be expressed [39] as:

$$\tilde{\alpha}[Q_1(1)] = \frac{16\pi^3}{5ha^8} \xi S g^2 \langle 00 | \alpha | 00 \rangle^2 \langle v1 | Q_2(r) | 01 \rangle^2 \quad (3)$$

where  $S$  is  $\sum_{i,j} (a^2/a_i a_j)^4 P_3(\cos \theta_{ij}) = 0.3062$  [41];  $\alpha$  is the isotropic polarizability, and  $g$  is a correction factor arising from the fact that the excited  $v$  state is not completely localized [64]. Eq. (3) is same as the intensity formula given by Sears and Van Kranendonk [64] with a lattice sum in a slightly different form. Using in Eq. (3) the most accurate values of the matrix elements [56,57], we get  $\tilde{\alpha}[Q_1(1)] = 1.03 \times 10^{-15}$  cm<sup>3</sup>/s, which is 1.85 times smaller than that of Ref. [64]. Note also that even with the (less accurate) parameters given in Ref. [64] one calculates  $\tilde{\alpha}[Q_1(1)] = 1.19 \times 10^{-15}$  cm<sup>3</sup>/s (just 15% higher than our theoretical value). Presumably, in Ref. [64], this value had been misprinted as  $\tilde{\alpha}[Q_1(1)] = 1.9 \times 10^{-15}$  cm<sup>3</sup>/s. Due to the incorrect theoretical intensity of the  $Q_1(1)$  transition  $m$  given in Ref. [64], the *ortho*-H<sub>2</sub> concentrations determined by the Winnewisers' group in their experiments are underestimated by a factor of ~1.85. Therefore, the experimental intensities of the transitions involving *ortho*-H<sub>2</sub> need to be divided by 1.85 in Refs. [17,18,21–23]. This resolution of the above-mentioned discrepancy leads to better overall agreement between the experimental and theoretical values of  $\tilde{\alpha}$  for  $[\Delta J = \ell]_v(1)$  transitions. We also point out that Varghese et al. [15] have not used the correct number density of the absorbing



species to calculate the integrated absorption coefficients for double transitions involving *ortho*–*para* pair (mixed transition). For a mixed transition the number density of absorbing species  $N = N_{ortho}N_{para}/(N_{ortho} + N_{para})$  should be used, not the total number of hydrogen molecules per  $\text{cm}^3$ , as used in Ref. [15]. Therefore, the value of  $\tilde{\alpha}$  given in Table 3 is 100 times the value reported in Ref. [15], to account for the correct density of absorbing species ( $\sim 1\%$  *ortho*-H<sub>2</sub> concentration). In this context, we note that it is better for experimental values of  $\alpha$  not  $\tilde{\alpha}$  (or both) to be reported.

After including the corrections for *ortho*-H<sub>2</sub> concentration, the experimental and theoretical intensities (assuming  $\xi = 1$ ) for the pure rotational and fundamental rovibrational transitions given in Table 1 agree within 60%, except for the extremely weak *Y* transitions. Here it is important to mention that experimental inaccuracy itself in most of the cases is  $\sim 20\%$  but there are appreciable differences between independent experimental determinations. This shows that setting the values of phonon renormalization factors  $\xi$  to unity in the calculation of theoretical intensities is not a serious source of error, except for the  $S_v(J)$  transitions. However, a good knowledge of  $\xi$  would certainly improve the accuracy of theoretical intensities. For overtone single transitions, the disagreement between theory and experiment is, in most cases, greater than a factor of 4. Most of this discrepancy can be attributed to the inaccuracy of the theoretical matrix elements due to their intrinsically small magnitudes (for overtone transitions the matrix elements of multipole moments become quite small and a loss of significant figures occurs). One case that merits special mention here is the  $U_2(0)$  transition for which the theoretical intensity is approximately two orders of magnitude smaller than the experimental intensities (see Table 1). The magnitude of the calculated hexadecapole moment matrix element for this transition is  $6 \times 10^{-4}$  in atomic units [57], which is comparable to (in fact larger than) the uncertainty in the  $r$ -dependent multipole moment function [64].

The large differences between the experimental and theoretical values of  $\tilde{\alpha}$  for *Y* transitions, as seen in Table 1, are partly due to larger experimental errors. The zero-phonon transitions in *para*-H<sub>2</sub> crystals become narrower and narrower as the value of  $\Delta J$  increases [16,31]. By extrapolating the linewidths and multipole moments from  $\Delta J = 2, 4$  and 6 transitions, Chan et al. [31] predicted the FWHM of  $Y_0(0)$  to be about 10 MHz ( $3 \times 10^{-4} \text{ cm}^{-1}$ ), and the transition  $2^8$ -moment to be  $0.189 ea_0^8$  (in good agreement with the value  $0.155 ea_0^8$  computed later [57]). However, the FWHM of the  $Y_0(0)$  transition observed by Steinhoff et al. [17] is  $0.0099 \text{ cm}^{-1}$ , larger by a factor 33 compared to the estimated value of Ref. [31]. The observed linewidth of the  $Y_0(0)$  transition is even larger than that of the  $W_0(0)$  transition, viz.  $0.003 \text{ cm}^{-1}$  [16]. (Note in Table 2 of Ref. [17] this is incorrectly given as  $0.02 \text{ cm}^{-1}$ ). In addition, from the observed intensity of the  $Y_0(0)$  transition in Ref. [17], one gets the transition moment as  $0.716 ea_0^8$ , which is larger by a factor  $\sim 4$  than the predicted or the computed transition

moment [31,57]. A similar situation for the linewidth and transition moment is found for the measured  $Y_1(0)$  transition [21]. Because the linewidths of the *Y* transitions seem to be instrumentally limited, this may give rise to large uncertainties in intensity measurements. Uncertainty in the ‘effective’ path length of multipass absorption cells may be another factor contributing to the accuracy of measured intensities. Steinhoff et al. [17] obtained an effective path length of only 2.4 times the single pass length for seven passes through the cell. This estimate was arrived at by comparing the intensity of the  $Q_1(1)$  transition in the single and multipass experiments. The  $Q_1(1)$  transition is relatively strong and the absorption spectrum may suffer from nonlinear (saturation) effects, which may influence the multipass measurements; this also could severely affect the measured intensities and consequently, the estimated path lengths.

From the results presented in Table 2 for the double transitions in *para*-H<sub>2</sub>, one can see that there is reasonable overall agreement between theory and experiment, even for some of the overtone transitions involving  $U_v(0)$ . Because the lattice sums for double transitions do not have the cancellation effect, the effects of phonon renormalization are less important in this case. We also include theoretical estimates for some yet unobserved transitions, many involving the higher  $\Delta J$ . Finally, after revising the experimental values as explained above, the results for the mixed double transitions (Table 3) are in reasonable agreement with the theoretical values.

#### 4. Conclusions

From the comparison between theory and experiment, we are able to draw the following conclusions. The range of experimental integrated absorption coefficients varies by a factor of  $10^8$ , where the weakest transitions were measured by the Winniewissers’ group. This feat was accomplished by their ability to grow larger crystals of *para*-H<sub>2</sub> and their use of a multipass arrangement. Over this very large dynamic range, the agreement between theory and experiment is rather good, especially after some of the corrections to the previously published values are made as discussed in Section 3. By considering experimental and theoretical ratios of specific transitions, one can check for consistency, and differentiate between phonon renormalization effects and those arising from inaccuracies in the theoretical multipole moment matrix elements. Improvements with respect to both of these aspects are a challenge for theory. Other effects not discussed in detail here, such as crystal-field splittings and line widths, are also challenging theoretical problems. On the other hand, with theoretical estimates for the absorption coefficients for higher-order  $\Delta J$  transitions, there is a challenge to experimentalists to improve the sensitivity of experimental measurements, and to observe some of these weaker transitions. Although, it would be rash to say that the experimental determination

of the higher ( $\ell \geq 6$ ) multipole moments of the hydrogens cannot be made by other techniques, it is clear that solid hydrogens are the ideal media and offer the best prospect in the near future.

### Note added in proof

From correspondence with the Winnewissers after the paper was submitted, we would like to make the following points in reference to the text. First, the effective path length was realized as an important source of error in the experimental value of  $\alpha$ . Second, the experimental width for the  $W_0(0)$  transition given in Table 2 of Ref. [17] was correctly reported and not a misprint as suggested in the text. The large value may be attributed to the thermal inhomogeneity of the large crystal (vertical gradient). At a temperature of 12.5 K, a typical thermal gradient of 0.2 K is sufficient to smear the peak over  $0.01 \text{ cm}^{-1}$ , consistent with the value reported.

### Acknowledgements

One of the authors (A.P.M.) thanks Dr N.C. Das, Head, Spectroscopy Division, BARC for his keen interest in this work. Two of the authors (R.H.T. and Q.M.) acknowledge financial support from NASA under grant NAG5-13337.

### References

- [1] J. Van Kranendonk, Solid Hydrogen, Plenum Press, New York, 1983.
- [2] T. Oka, Annu. Rev. Phys. Chem. 44 (1993) 299.
- [3] I.F. Silvera, Rev. Mod. Phys. 52 (1980) 393.
- [4] J. Van Kranendonk, Can. J. Phys. 38 (1960) 240.
- [5] H.P. Gush, J. Phys. Radium 22 (1961) 149.
- [6] A. Crane, H.P. Gush, Can. J. Phys. 44 (1966) 373.
- [7] J. Van Kranendonk, G. Karl, Rev. Mod. Phys. 40 (1968) 531.
- [8] R.D.G. Prasad, M.J. Clouter, S. Paddi Reddy, Phys. Rev. A 17 (1978) 1690.
- [9] T.K. Balasubramanian, C.-H. Lien, K. Narahari Rao, J.R. Gaines, Phys. Rev. Lett. 47 (1981) 1277.
- [10] K. Ivancic, T.K. Balasubramanian, J.R. Gaines, K. Narahari Rao, J. Chem. Phys. 74 (1981) 1508.
- [11] C.K.N. Patel, E.T. Nelson, R.J. Kerl, Phys. Rev. Lett. 47 (1981) 1631.
- [12] C.Y. Kuo, M.M.F. Vieira, R.J. Kerl, C.K.N. Patel, Phys. Rev. Lett. 50 (1983) 256.
- [13] K. Narahari Rao, J.R. Gaines, T.K. Balasubramanian, R. D'Cunha, Acta Phys. Hung. 55 (1984) 383.
- [14] I. Glatt, R.J. Kerl, C.K.N. Patel, Phys. Rev. Lett. 57 (1987) 1437.
- [15] G. Varghese, R.D.G. Prasad, S.P. Reddy, Phys. Rev. A 35 (1987) 701.
- [16] M. Okumura, M.-C. Chan, T. Oka, Phys. Rev. Lett. 62 (1989) 32.
- [17] R.A. Steinhoff, B.P. Winnewisser, M. Winnewisser, Phys. Rev. Lett. 73 (1994) 2833.
- [18] R.A. Stienhoff, K.V.S. Apparao, D.W. Ferguson, K. Narahari Rao, B.P. Winnewisser, M. Winnewisser, Can. J. Phys. 72 (1994) 1122.
- [19] D.P. Weliky, T.J. Byers, K.E. Kerr, T. Momose, R.M. Dickson, T. Oka, App. Phys. B 59 (1994) 265.
- [20] R.M. Dickson, T. Oka, J. Phys. Chem. 99 (1995) 2617.
- [21] M. Mengel, B.P. Winnewisser, M. Winnewisser, Phys. Rev. B 55 (1997) 10420.
- [22] M. Mengel, B.P. Winnewisser, M. Winnewisser, J. Mol. Spectrosc. 188 (1998) 221.
- [23] M. Mengel, B.P. Winnewisser, M. Winnewisser, J. Low Temp. Phys. 111 (1998) 757.
- [24] S.B. Baliga, R. Sooryakumar, K. Narahari Rao, R.H. Tipping, J.D. Poll, Phys. Rev. B 35 (1987) 9766.
- [25] M.C. Chan, T. Oka, J. Chem. Phys. 93 (1990) 979.
- [26] P.C. Souers, J. Fuentes, E.M. Fearon, P.E. Roberts, R.T. Tsugawa, J.L. Hunt, J.D. Poll, J. Chem. Phys. 72 (1980) 1679.
- [27] P.C. Souers, D. Fearon, R. Garaza, E.M. Kelly, P.E. Roberts, R.H. Sanborn, R.T. Tsugawa, J.L. Hunt, J.D. Poll, J. Chem. Phys. 70 (1979) 1581.
- [28] K.K. Lo, PhD Dissertation, The Ohio State University, Columbus, USA, 1983.
- [29] K. Narahai, Rao, J. Mol. Struct. 113 (1984) 175.
- [30] S.Y. Lee, PhD Dissertation, The Ohio State University, Columbus, USA, 1987.
- [31] M.-C. Chan, S.S. Lee, M. Okumura, T. Oka, J. Chem. Phys. 95 (1991) 88.
- [32] J.D. Poll, R.H. Tipping, Can. J. Phys. 56 (1978) 1165.
- [33] Q. Ma, R.H. Tipping, J.D. Poll, Phys. Rev. B 39 (1989) 132.
- [34] R.H. Tipping, Q. Ma, J.D. Poll, T.W. Noh, S.Y. Lee, S.-I. Lee, J.R. Gaines, Phys. Rev. B 38 (1988) 6440.
- [35] R.H. Tipping, J.D. Poll, S.-I. Lee, T.W. Noh, S.Y. Lee, J.R. Gaines, Phys. Rev. B 39 (1989) 6514.
- [36] J.D. Poll, M. Attia, R.H. Tipping, Phys. Rev. B 39 (1989) 11378.
- [37] J.D. Poll, R.H. Tipping, S.Y. Lee, S.-I. Lee, T.W. Noh, J.R. Gaines, Phys. Rev. B 39 (1989) 11372.
- [38] T.K. Balasubramanian, R. D'Souza, R. D'Cunha, K. Narahari Rao, Can. J. Phys. 67 (1989) 79.
- [39] T.K. Balasubramanian, R. D'Souza, R. D'Cunha, K. Narahari Rao, J. Mol. Spectrosc. 153 (1992) 741.
- [40] A.P. Mishra, T. K. Balasubramanian, Phys. Rev. B 59 (1999) 6002.
- [41] A.P. Mishra, R.W. Field, S.V.N. Bhaskara Rao, R. D'Souza, T.K. Balasubramanian, Phys. Rev. B 67 (2003) 134305.
- [42] A.P. Mishra, R.W. Field, Phys. Rev. B., submitted for publication.
- [43] R.J. Hinde, Phys. Rev. B 61 (2000) 11451.
- [44] J.C. McLennan, J.H. McLeod, Nature (London) 123 (1929) 160.
- [45] E.J. Allin, W.F.J. Hare, R.E. MacDonald, Phys. Rev. 98 (1955) 554.
- [46] E.J. Allin, T. Feldman, H.L. Welsh, J. Chem. Phys. 24 (1956) 1116.
- [47] J.D. Poll, J. Van Kranendonk, Can. J. Phys. 40 (1962) 163.
- [48] R.H. Tipping, Q. Ma, J.D. Poll, Phys. Rev. B 44 (1991) 12314.
- [49] S.P. Reddy, F. Xiang, G. Varghese, Phys. Rev. Lett. 74 (1995) 367.
- [50] R.H. Tipping, J.D. Poll, Phys. Rev. B 35 (1987) 6699.
- [51] C.G. Gray, J. Phys. B 4 (1971) 1661.
- [52] G. Karl, J.D. Poll, L. Wolniewicz, Can. J. Phys. 53 (1975) 1781.
- [53] J.D. Poll, L. Wolniewicz, J. Chem. Phys. 68 (1978) 3053.
- [54] J.L. Hunt, J.D. Poll, L. Wolniewicz, Can. J. Phys. 62 (1984) 1719.
- [55] J. Komasa, A.J. Thakkar, Mol. Phys. 78 (1993) 1039.
- [56] J. Rychlewski, Mol. Phys. 41 (1980) 833.
- [57] A.P. Mishra, T.K. Balasubramanian, Mol. Phys. 90 (1997) 895.
- [58] A.P. Mishra, T.K. Balasubramanian, Mol. Phys. 98 (2000) 967.
- [59] A.P. Mishra, S.V.N.B. Rao, T. K. Balasubramanian, Mol. Phys. 99 (2001) 721.
- [60] S.V.N.B. Rao, A.P. Mishra, R. D'Souza, T.K. Balasubramanian, J. Quant. Spectrosc. Radiat. Transfer, submitted for publication.
- [61] C. Schwartz, R.J. Le Roy, J. Mol. Spectrosc. 121 (1987) 420.
- [62] U. Bountempo, S. Cunsolo, P. Dore, L. Nencini, Can. J. Phys. 60 (1982) 1422.
- [63] S. Tam, M.E. Fajardo, Appl. Spectrosc. 55 (2001) 1634.
- [64] V.F. Sears, J. Van Kranendonk, Can. J. Phys. 42 (1964) 980.